

### THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.:

10/789,899

Filing Date:

February 27, 2004

Applicant:

Frederick E. Pinkerton et al.

Group Art Unit:

1754

Examiner.

Wayne A. Langel

Title:

MIXED HYDROGEN GENERATION MATERIAL

Attorney Docket:

GP-303644 (8540R-000058)

# DECLARATION OF PRIOR INVENTION IN THE UNITED STATES TO OVERCOME CITED PATENT PUBLICATIONS PURSUANT TO 37 C.F.R. §1.131

#### PURPOSE OF DECLARATION

- 1. I am a ∞-inventor of the patent application identified above and of the subject matter described and claimed therein, including of Claims 1 through 52.
- 2. This declaration is being presented to establish conception and reduction to practice of the Invention of the patent application identified above in the United States at a date prior to June 25, 2003.

#### **FACTS & DOCUMENTARY EVIDENCE**

3. Prior to June 25, 2003, having earlier conceived of the concept of storing hydrogen by reacting a nitride with a hydride, I submitted a record of invention to the legal department at General Motors Corporation. To establish the date of conception of the invention of the claims of this patent application, the attached record of invention document is submitted as Exhibit A. The redacted portions of Exhibit A either disclose dates that are all prior to June 25, 2003 or disclose personal confidential information. This document (hereinafter referred to as the "ROI"), was: prepared prior to June 25, 2003; Identifies me as one of the co-inventors; and discusses and Illustrates the conceived invention. The ROI Includes

a description of an example of hydrogen storage compounds where hydrogen gas is released by reacting a nitride compound and a hydride compound to form one or more byproduct compounds. The ROI further includes summary pages and various graphs illustrating various embodiments of the invention described in the application, as well as hand-written lab note pages further evidencing conception of the invention.

4. Our invention was reduced to practice and experiments were conducted to generate data detailed in Figures 1 - 5 of the above identified patent application and in the lab notebook pages describing experimental details regarding nitride and hydride systems (attached as Exhibit B). The redacted portions of Exhibit B are dates that are all prior to June 25, 2003. The detailed description of the above identified patent application (at Paragraphs 35-46) details how the data was generated to create Figures 1-5, respectively. To establish the date of reduction to practice of the subject matter as claimed in this patent application, Exhibit B contains laboratory notebook information illustrating reduction to practice prior to June 25, 2003.

#### DECLARATION

5. As the person signing below I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

#### **SIGNATURE**

Dated: Dez. 14, 2006

Martin S. Meyer

## **EXHIBIT A**

37 C.F.R. §1.131 Declaration of Martin S. Meyer U.S.S.N. 10/789,899 entitled "Mixed Hydrogen Generation Material."

Research & Development and Planning

Date:

Subj: R&D and Planning & NAPD Record of Invention File No. GP-303644

To: Kathryn A. Marra
GM Corporation Legal Staff

300 Renaissance Center M.C. 482-C23-B21 P.O. Box 300

Detroit, MI 48265-3000

Attached is the Record of Invention entitled "Mixed Hydrogen Generation Material" in the name(s) of Frederick E. Pinkerton (430), Martin S. Meyer (430), and Gregory P. Meisner (430).

Carol E. Siino Manager, Intellectual Property M.C. 480-106-359 810/986-2520

#### Attachment

C: Materials & Processes (430)



File No.

68.303644

## RECORD OF INVENTION

This Record of Invention must be completed with sufficient detail so that your invention can be understood and evaluated by both your engineering management and by a GM Legal Staff patent attorney. Novelty and competitive significance of your invention will be evaluated based on the information you provide.

Inventor #1 ame: Frederick	E	Pinkerton		Citizen of: USA	
First Name ocial Security No.	Middle Initial	Last N GM Employee:	ame ⊠ Yes □ No	Salary Hour	ly Contract
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Inventor #2*  Iame: Martin		Meyer		Citizen of: USA	
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				Phone No.	
Non-GM Employer:					(Area Code) + Number
Non-GM Employer Address:	Str	rect.	Cit	ly and State	Zip Code

File Number.

### Answer questions 1 - 8, completing all of them to the best of your knowledge. This invention was first thought of on: This invention has been or is expected to be disclosed outside GM on: This invention has been used or is committed to be used in production on: This invention has been offered for sale outside GM on: ☐ Yes 🛛 No Was this invention made while working on a Government Contract? 5. If yes, identify the government Contract No. Identify the product or process in which the invention is incorporated: Hydrogen Storage, Fuel Cells 6. List all individuals who can provide information about the making of the invention. This list may include individuals who made the first sketch, description, or tests and individuals who are familiar with the facts relating to the making of the invention. Frederick E. Pinkerton, Martin S. Meyer, Jan F. Herbst, John Vajo, Gregory P. Meisner, Michael P. Balogh 8. Each inventor has a legal duty to disclose all information known that is material to patentability of this invention. Such information includes the relevant prior art, which may be in the form of current or past products, equipment, processes, materials, patents, publications, advertisements, displays, and unpublished developments and proposals—whether originated by you, others in GM, competitors, suppliers, customers or others. Such information also includes disclosure of this invention outside GM, sales and offers of products using this invention, use of this invention in production and disputes about who should be considered as an inventor of this invention. To comply with the duty to disclose, list here and attach a copy of all such information, to the extent known. LiBH4 is known to be a "hydrolysis hydride" which will release hydrogen on exposure to water. Considerable work has been done on this material by Scott Jorgensen and collaborators at GM R&D and by other investigators elsewhere. A previous record of invention, GP-302578, has been submitted on reversible hydrogen storage in the Li-N-H system according to the formula $LiNH_2 + LiH <-> Li_2NH + H_2$ . A Microsoft PowerPoint presentation authored by John Vajo described his work at HRL on several coupled hydride compounds, namely LiOH+LiH, LiOH+NaH, LiH+Si, and MgH2+Si. He has also previously discussed LiBH4+MgH2 Greg Meisner has previously examined the mixtures LiAIH4 + LiNH2 and LiAIH4 + 4 LiNH2 for the purpose of using the LiH

REDACTED



produced from decomposition of LiAIH, to combine with the LiNH2 as above.

### Answer question 9 thoroughly.

<b>9.</b>	Describe the invention in sufficient detail so that its nature, operation and usefulness can be understood.  (Attach drawings, diagrams and further description, when necessary. Additional guidelines are listed below.)
	See attached.
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	Mechanical and Electrical Devices: Include illustrations assigning reference numbers to the main elements and refer to the reference numbers in a description that explains how the main elements are connected or related and how they operate.
	Electrical Circuits and Controls: Include circuit diagrams and a functional description.  Computer Software and Manufacturing or Business Processes: Include a flowchart or other step-by step overview.
	<u>Chemical Inventions:</u> Identify all essential materials used, and alternatives therefor, in chemical terms — not tradenames. Identify and quantify all significant variables (e.g. temperature, pressure, concentration, pH etc.) of the process or material specifying operating ranges and the preferred example. Discuss the significance of each variable. Provide a recipe for at least one working example of the invention.
g:	PEDACTER
316	File Number: NEUACIED

# I hereby assign this invention to General Motors Corporation and authorize General Motors Corporation to file an application on my behalf.

Arederick E. Pinkerton	Frederick E. Pinkerton (ALSO, PRINT NAME)	
INVENTOR - SIGNATURE	(ALSO, PRINT NAME)	DATE
Martin & Meyn INVENTOR-SIGNATURE	Martin S. 977eyer (ALSO, PRINT NAME)	DATE
Theory Magne	GRESSRY P. MEISNER	
INVENTOR-SIGNATURE	(ALSO, PRINT NAME)	DATE
, O		
This invention was reviewed and understood b	by me:	
Jan F. Herbst 1 WITNESS-SIGNATURE	Jan F. Herbst (ALSO PRINT NAME)	DATE
What P. Balax	Michael P. Balogh	DATE
2 <sup>nd</sup> WITNESS'-SIGNATURE	(ALSO, PRINT NAME)	DATE

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File Number

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## Answer the following questions if helpful in describing this Invention

	Answer the following questions in only in
0.	What benefits will be realized by using this invention?
	The benefit of this invention is as a source of hydrogen for fuel cell applications.
	What is the state of development of this invention?
11.	
	Hydrogen generation has been successfully demonstrated in LiBH <sub>4</sub> + 2 LiNH <sub>2</sub> with an onset temperature of 100 $^{\circ}$ C and bulk hydrogen release at a temperature of 245 $^{\circ}$ C.
12.	To the extent known, what alternatives exist for accomplishing substantially the same result as this invention?
	Hydrogen can be stored as a compressed gas, as a cryogenically cooled liquid, or in a solid. Current solid storage media lack hydrogen capacity, have slow kinetics, or require high or low temperatures. Hydrogen release in LiBH4 can be accomplished by addition of water or water vapor, but with a weight penalty due to the additional weight of the water.
	$oldsymbol{\cdot}$
13.	in the prior art that are overcome by this invention.
	A survey of the literature revealed the existence of Li <sub>3</sub> BN <sub>2</sub> ; this invention resulted from considering Li <sub>3</sub> BN <sub>2</sub> as the reaction product of a mixture of other hydrogen containing compounds, such as LiBH <sub>4</sub> + LiNH <sub>2</sub> , thereby releasing hydrogen gas.
	The binary couple LiNH $_2$ + LiH has been the subject of a previous Record of Invention.
	Conventionally, LiBH $_4$ is known as a hydrolysis hydride, in which hydrogen is released by exposure to water.
	Thermal decomposition of LiBH <sub>4</sub> is impractical, requiring a temperature of $-400$ °C, and at that temperature it releases B-H compounds in addition to $H_2$ .
	REDACTED
A	Cir. Number

File Number:

#### Inventor # 3

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GM Uni	it: <u>GM</u>	Research and Deve	hopment Center			Centrex Number	(Area Code) + Number
		20500 ) 6 3 73 d	Warran MT 4809	0-9055 Mail Code	480-106-224	FAX Number:	(8)-226-3091
GM Ad	dress:	30500 Mouna Ka.	, Warren, MI 4809	<u> </u>			Centrex Number
	1					Phone No.	
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NOD-GI	M Employ	er Address:	Str	eet	City	and State	Zip Codc
In	ventor#					Citizen of:	
Name:				Last Na	·	Citizen or.	
		First Name	Middle Initial			Salary Hou	rly Contract
Social S	Security N	٥.		GM Employee:	∐ Yes ∐ No	المالية المالية	., _
Home A	Address:						71.0-4.
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GM Un	nit:				GM Phone No.	(8)-	(Arca Code) + Number
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This invention describes an example of coupled hydrogen storage compounds in which hydrogen gas is released by hearing a mixture of two compounds, at least one of which contains hydrogen. The chemical reaction considered here is given by:

 $LiBH_4 + 2 LiNH_2 \rightarrow Li_3BN_2 + 4 H_2$ 

The theoretical amount of hydrogen released is 11.8 wt% of the starting hydride mixture.

Hydrogen release has been demonstrated as shown in the accompanying figures.

In the first experiment, a mixture of LiBH4 and LiNH2 of molar ratio 1:2 was used according to the above chemical reaction formula. The mixture was ground together in an inert atmosphere using an agate mortar and pestle. A sample weighing 1.102 grams was loaded into the sample holder of the PCI apparatus and all the spaces were Then the temperature was increased and pressure measurements were recorded until the sample temperature reached -400°C. Figure 1 shows the sample temperature and hydrogen desorption versus time. We note a slight decrease in the gas pressure between 10 and 25 hours, Figure 2, which could indicate a small amount of reabsorption of the desorbed gas. The pressure of the desorbed gas reached about 900 kPa in this experiment corresponding to a hydrogen weight per cent desorption of about 3.06 wt%. Subsequently, the sample was cooled to ~50°C and the desorbed gas evacuated. A second heating cycle was performed, Figure 3, and another small amount of gas desorbed. Figure 4 shows a composite of the two experimental results showing a total desorption of 3.21 wt% hydrogen. The onset of the desorption as a function of temperature, shown in Figure 5, is approximately 100°C. Finally, we attempted to absorb hydrogen back into this sample by pressurizing up to >9000 kPa at 200°C. Figure 6, however, shows no hydrogen uptake to within the experimental uncertainty of the PCI apparatus. Subsequent x-ray diffraction analysis, Figure 7, revealed that this sample was heavily oxidized and contained mostly Li<sub>2</sub>O and Li<sub>3</sub>BO<sub>3</sub>.

In the second experiment, LiBH4 and LiNH2 were mixed in a 1.18:2 molar ratio (the excess LiBH4 is the result of a weighing error) and ball milled for 10 minutes in a steel vial using a SPEX 8000 mixer/mill. Some of the resulting powder was placed into a thermograyimetric analyzer (TGA), where hydrogen release appears as weight loss of the sample as shown in the upper panel of Figure 8. The mixture was heated in stages up to 245°C under 1.3 atm flowing He gas, and at temperatures > 200°C lost weight totaling 13.5 wt%. A mass spectrometer operated as a residual gas analyzer (RGA) was used to monitor the composition of the exhaust gas, as shown in the lower panel of Figure 8. The broad humps in the RGA signal from all species during heating reflect a general change in the background signals of all the species related to heating the TGA, and these are unrelated to the sample. Alone among them, H2 gas shows a large excess concentration strongly correlated with heating events. The sharp drop in the H2 mass spectrometer signal at the end of the TGA weight loss is particularly dramatic. A semi-quantitative analysis of the amount of H2 released gives 11.8 wt% (the exact correspondance with the chemistry above must be regarded as somewhat fortuitous). X-ray diffraction analysis of the starting ball-milled mixture is shown in Figure 9. The red bars indicate the expected



diffraction lines from LiNH<sub>2</sub> and the green bars are the expected lines from LiBH<sub>4</sub>. The presence of large diffraction lines, particularly at 20 ~16°, ~21°, and ~29°, shows that ball-milling has largely transformed the starting compounds into another compound that we have not yet been able to identify. A minor amount of Li<sub>2</sub>O is also present as an impurity, and it is most likely an inert diluent. Figure 10 shows the x-ray diffraction pattern obtained after desorption of >10 wt% hydrogen in the TGA. The dominant phase is the expected Li<sub>3</sub>BN<sub>2</sub> compound, but one or more additional phases (along with the impurity Li<sub>2</sub>O phase) are also present, as indicated by the as yet unidentified extra diffraction lines. In contrast to the first sample, this sample after desorption is not heavily oxidized.

By itself LiBH<sub>4</sub> melts at ~280°C, but does not decompose with significant weight loss until ~400°C. By itself LiNH<sub>2</sub> decomposes slowly at 200°C and above, and at rates comparable to those observed in the example, but it does so by releasing ammonia rather than H<sub>2</sub>. If this mechanism were responsible for the weight loss, the total loss should be 25 wt%. The example shows that when the two materials are combined via ball milling, the mixture decomposes by H<sub>2</sub> release at ~245°C.

Preliminary attempts to reverse the reaction, thereby providing a reversible hydrogen storage medium, were not successful. Efforts to make the reaction reversible continue, however. Incorporating a catalyst is one method known to both reduce the hydrogen release temperature and facilitate reabsorption in other hydrogen storage materials, and we expect that it will work for this invention as well.

A number of similar reactions can be written

```
\begin{split} \text{LiAlH}_4 + 2 \, \text{LiNH}_2 &\rightarrow \text{Li}_3 \text{AlN}_2 + 4 \, \text{H}_2 \, \, \, (9.5 \, \text{wt\%}) \\ \text{NaBH}_4 + 2 \, \text{NaNH}_2 &\rightarrow \text{Na}_3 \text{BN}_2 + 4 \, \text{H}_2 \, \, \, (6.9 \, \text{wt\%}) \\ 2 \, \text{LiBH}_4 + \text{Mg} &\rightarrow \text{MgB}_2 + 2 \, \text{LiH} + 3 \, \text{H}_2 \, \, (8.9 \, \text{wt\%}) \\ \text{Mg(BH}_4)_2 + 3 \, \text{Mg(NH}_2)_2 + 2 \text{Mg} &\rightarrow 2 \, \text{Mg}_3 \text{BN}_3 + 10 \, \text{H}_2 \, \, (7.4 \, \text{wt\%}) \\ \text{Mg(BH}_4)_2 + 3 \, \text{Mg(NH}_2)_2 + 2 \text{MgH}_2 &\rightarrow 2 \, \text{Mg}_3 \text{BN}_3 + 12 \, \text{H}_2 \, \, (8.7 \, \text{wt\%}) \\ \text{Mg(BH}_4)_2 + 6 \, \text{MgNH} &\rightarrow 2 \, \text{Mg}_3 \text{BN}_3 + \text{Mg} + 7 \, \text{H}_2 \, \, (4.8 \, \text{wt\%}) \\ \text{Mg(BH}_4)_2 + 6 \, \text{MgNH} &\rightarrow 2 \, \text{Mg}_3 \text{BN}_3 + \text{MgH}_2 + 6 \, \text{H}_2 \, \, (4.1 \, \text{wt\%}) \\ \text{Mg(BH}_4)_2 + 2 \, \text{Mg(NH}_2)_2 &\rightarrow \text{Mg}_3 \text{BN}_3 + \text{Mg}_4 + 8 \, \text{H}_2 \, \, (9.6 \, \text{wt\%}) \end{split}
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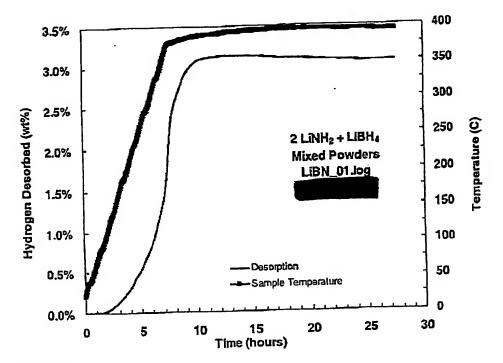


Figure 1

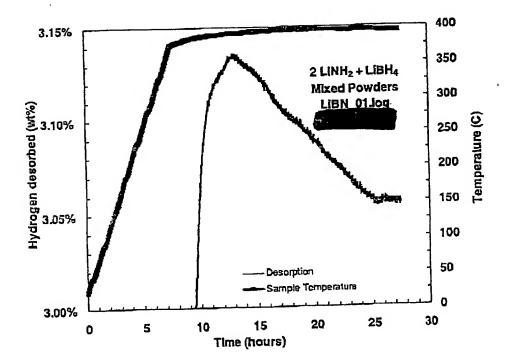


Figure 2

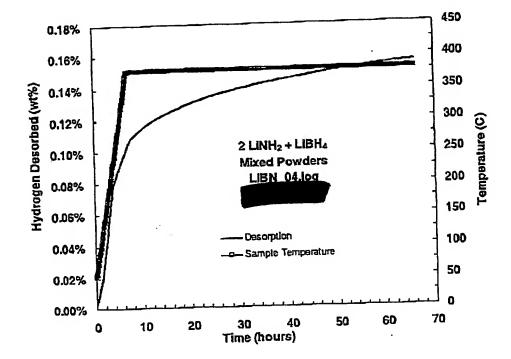


Figure 3

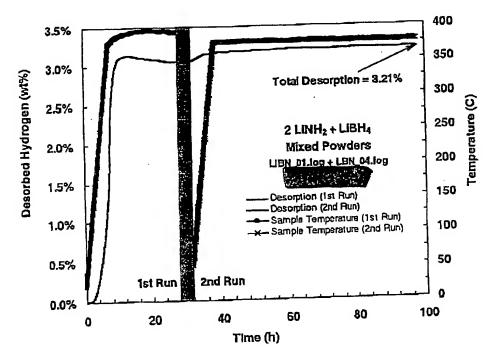


Figure 4

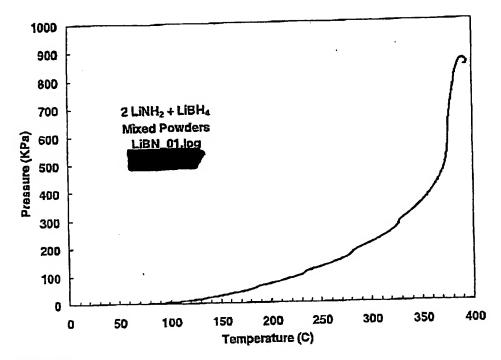


Figure 5

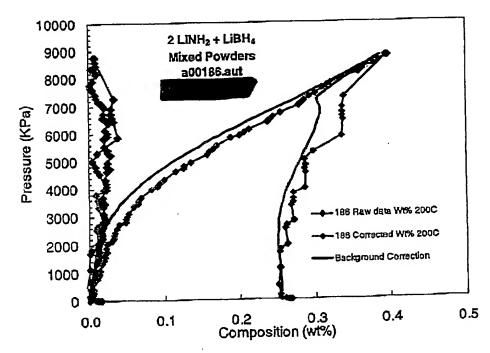
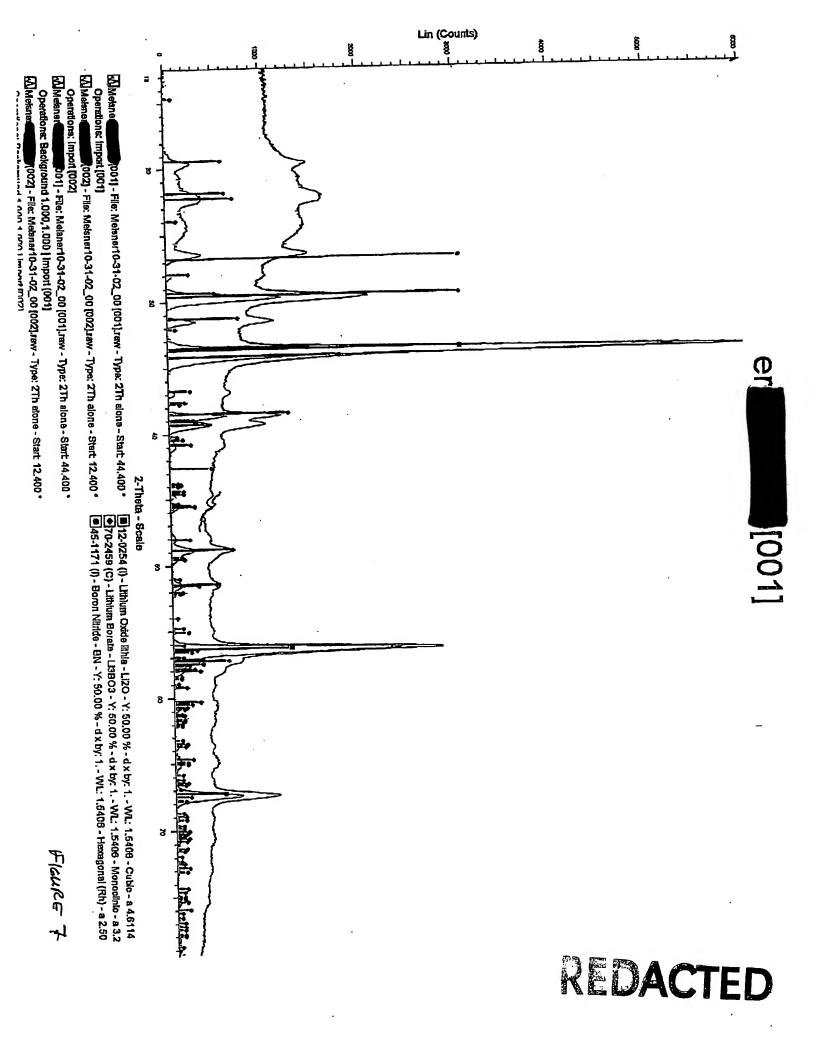


Figure 6



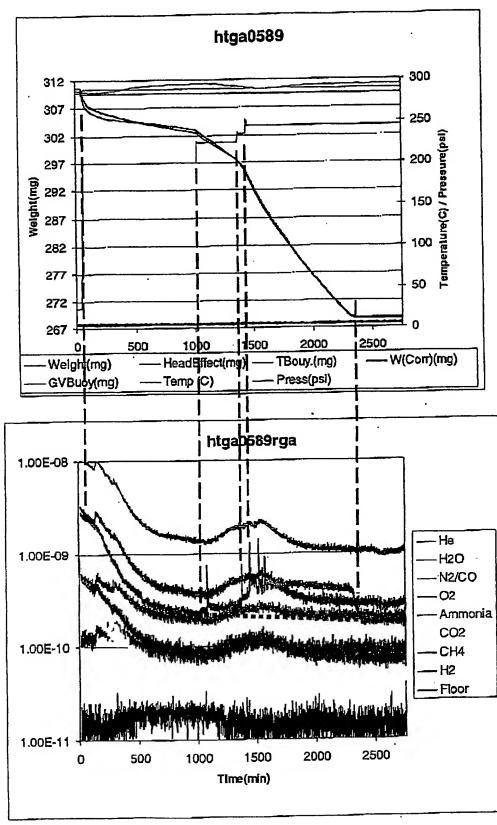


Figure 8

## P886 P886 Mech.Alloy HSP075-10m LiBH₄ + 2 LiNH₂ HEBM 10 min GADDS x-ray T series, scan 1: heating 39°C

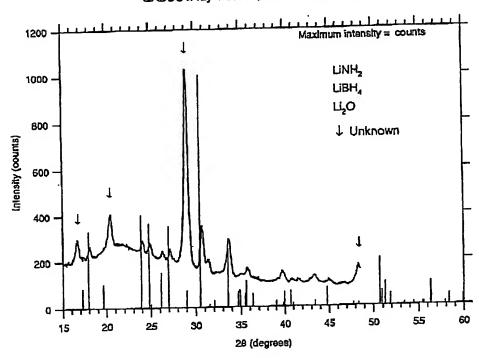
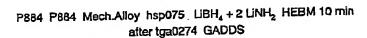


Figure 9



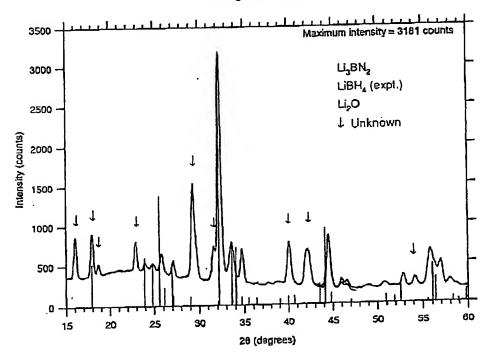
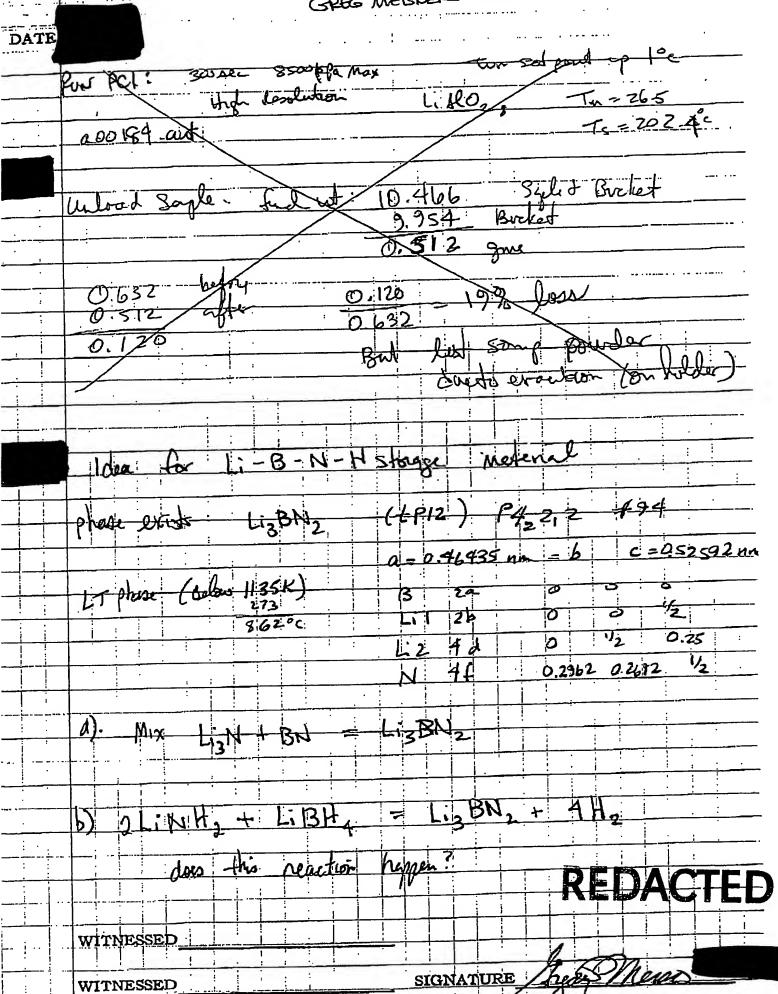


Figure 10

## **EXHIBIT B**

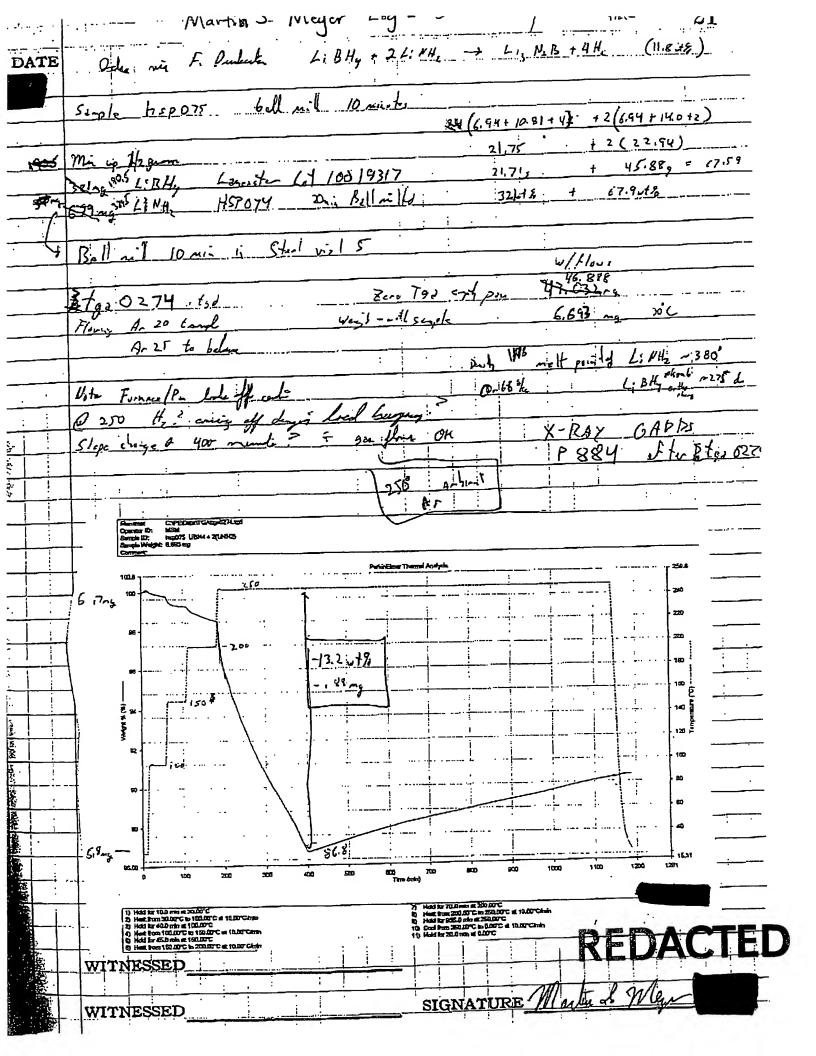
37 C.F.R. §1.131 Declaration of Martin S. Meyer U.S.S.N. 10/789,899 entitled "Mixed Hydrogen Generation Material."

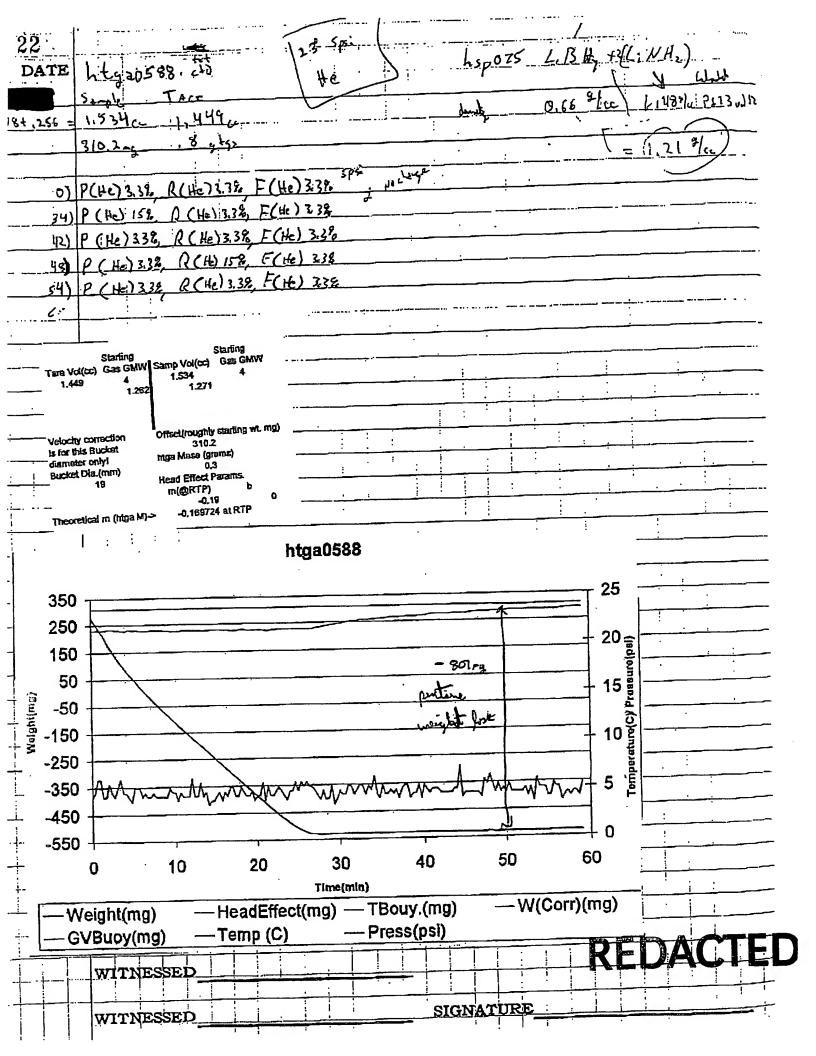


SIGNATURE

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DATE	(7.37 wt%)
<b>5</b>	2 Mg + Mg (BH4) 2 + 3 Mg (NH2) 2 = 2 Mg 3 BN3 + 10 H2
6	2 Mg H2 + Mg (BH4)2 + 3 Mg (NH2)2 = 2 Mg , BN3 + 12 H2 (8.71 ~ 196)
	From Mg imide: 14.83 270 marrier MANN)
ð	Mg (BH4) 2 + 6 Mg NH = 2 Mg 3 BN3 + Mg +7 MH2
8	Ma(BH4) + 6 MaNH = 2 Ma 3 BN 3 + MgH2 + 1 H2 (4,14)
	Reactions 5+6 are 3-component reactions, and thus may be difficult or slow in practice.
	JCPDS also lists Mg B Ny but as Q (questionable)  IE this phase exists we could have
9_	Ma (BHu) + 2 Ma (NH2) = Ma 3 B2 N4 + 8 H2 (9.61 LA 6)
	Pearson's does not list any phases not already discussed
	Pearson's does not list any phases not already disassed. There are no listings for Nd-Al-N or Mg-Al-N  There are no listings for Nd-Al-N or Mg-Al-N  phases in the databases If such unknown phases  were to exist, Al cognates might be possible.
	viere to exist. Al coquates might be possible.
	Motor on readion 3): Greg Meisner tried a related
	reaction LiAltu + LiNH2 -> \$ LizAlto + 3Al + H2 + LINH2
. ;	-> 1; H + A1 + = H2 + LINH2
	-> LiNH + Al + EH2 (i-e use lith from
	He did not report any unusual more Ha)
	belieuror
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i	WITNESSED J. T. Peror.
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